Influence of curing conditions in air lime-metakaolin blended mortars – A mineralogical and mechanical study

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Abstract

The need to formulate mortar compositions with adequate durability and compatibility is nowadays one of the major challenges in historical buildings repair. The incorporation of pozzolanic materials as addition or replacement of lime is viewed as a solution to these challenges regarding the increase in hardening time, mechanical strength, water resistance and durability. This paper includes part of an extensive work being developed in Portugal, which has the objective of developing and characterizing lime-metakaolin mortars for conservation purposes. This paper evaluates the influence of the curing conditions, namely medium and high relative humidity (HR), lab and outdoor exposition, and direct daily contact with potable or sea water. Two air lime mortars with volumetric proportion 1/3 of binder and aggregate, with 0 and 9% metakaolin (mass % replacement of air lime) were characterized up to one year of age. The mortars evolution with curing was followed by XRD, TG-DTA, tensile and compressive strength tests. The humid and urban curing revealed the best results in terms of the pozzolanic reaction, occurring mostly at lower curing times (28 days), although carbonation reaction is dominant throughout all ages up to 1 year.

Keywords: air lime, metakaolin, repair mortar, curing condition, hardening reaction

1. Introduction

Mainly due to aging but often due to inadequate choice of the employed building materials, used in previous restoration interventions, masonry walls of historic buildings have become deteriorated. An adequate choice of repair mortars is thus critical to get through with a well succeeded restoration process. Compatibility has to be desirably reached between the original components of the masonry and new repair mortar. Thus, several aspects must be similar to the ancient ones, namely in terms of chemical, physical, structural and mechanical properties (Degryse et al. 2002, Elert et al. 2002, Hansen et al. 2007).

The use of air lime as binder in mortars involves well-known inconveniences, such as slow setting, long carbonation times and low mechanical strength. Nowadays, the addition of pozzolanic additions to air lime mortars is recommended because they confer good properties in the early age, higher values of mechanical strength, good cohesion between binders and aggregates and durability (Arrizi et al. 2012, Velosa et al. 2001, Charola et al. 2005).

This paper deals with the study of the influence of a high reactive aluminosilicate pozzolan, metakaolin (Mk), which is formed by the dehydroxilation of kaolinite at ~ 650-800ºC. Different curing conditions are evaluated due to its importance on the mechanical properties. Several physical and chemical tests, namely flexural and compressive strength, X-ray diffraction analysis (XRD) and simultaneously thermogravimetric and differential thermal analysis (TG-DTA), were conducted evaluating the evolution of the lime-Mk mortars' characteristics and composition in respect to time.

2. Experimental and methods

2.1 Materials and mortar preparation

Mortars were prepared by mixing a Portuguese commercial hydrated air lime powder EN 459-1 CL90 (Lusical H100 – designated by L) and a mixture of three different graded washed siliceous river sands as aggregate, with volumetric ratios of 1:3 (binder/aggregate). The lime binder was maintained or replaced by 9% wt. of commercial metakaolin (Argical M1200S – designated by Mk). Mix designs of the different mortars are given in table 1.

The procedure regarding the mixing process was the same for these two mortars. The dry constituents were manually homogenised and placed in the mechanical mortar mixer container. Water was added in the first seconds of mixing to achieve consistency for an adequate workability. The mixing went on for 150 seconds and another 30 seconds at low speed. The flow table consistency was determined based on EN 1015-3 and flow values of 150 ± 10 mm for all the mortars were obtained. The water/binder ratio was 2.6 for air lime mortars and 2.8 for air lime-Mk blended mortars.

After mechanical mixing and compaction, specimens were moulded in metallic prismatic moulds of 40 x 40 x 160 mm^3 and conditioned inside polyethylene bags during 6 days for initial curing with high RH. The mortars without Mk were not yet hardened enough to be demoulded and had to be kept for two more days outside the polyethylene bags to be demoulded. That situation clearly showed the difference on hardening of pure air lime mortars in comparison with air lime-Mk mortars. After removing the mortar samples from the moulds, they were maintained in different curing conditions and characterized at ages from 28 days up to 1 year. The six different curing conditions were named (i) H – humid curing (laboratory 90±5% RH and 20±3ºC), (ii) S - standard curing (laboratory 65±5% RH and 20±3ºC), (iii) U - urban curing (natural ambient exposure at LNEC near a busy road in Lisbon), (iv) M - maritime curing (natural ambient exposure not far from the coast at Nova University of Lisbon in Caparica), (v) PWS – potable water spray at standard curing, at standard condition (65% RH and 20±3ºC) plus daily spraying with potable water and (vi) MWS – maritime water spray at standard curing (65% RH and 20±3ºC), at standard curing plus daily spraying with sea water. The mortar mixes identification, curing type, volumetric and weight ratios and percentage of lime weight substitution by Mk are shown in Table 1.

Table 1: Curing type, mortar mixes, binder/aggregate (b/a) ratios and Mk replacement content.

Curing type	Mortar identification	b/a Volume	b/a Weight	Mk (wt. %)
Humid	H1	1/3.1	1/12.1	0
	H2	1/3.4	1/14	9
Standard	St1	1/3.1	1/12.1	0
	St2	1/3.4	1/14	9
Urban	U1	1/3.1	1/12.1	0
	U2	1/3.4	1/14	9
Maritime	M1	1/3.1	1/12.1	0
	M2	1/3.4	1/14	9
Potable water spray	PWS1	1/3.1	1/12.1	0
	PWS2	1/3.4	1/14	9
Maritime water spray	MWS1	1/3.1	1/12.1	0
	MWS2	1/3.4	1/14	9

During the first two weeks of unprotected exposure outside extreme conditions occurred: a week of high temperatures (around 30ºC) followed by a week of hard hailstorms. Some of the mortars in curing conditions M and U became damaged and maybe its hardening process was jeopardised. The damage was mainly the destruction of the exposed surface of the samples, reducing their section.

2.2 Flexural and compressive strength tests

Flexural and compressive strength tests were held following the EN 1015-11 standard. Three samples of each mortar/curing were tested at each age by a three points bedding flexural test with a 2 kN load cell in a Zwick equipment. The half samples from the flexural test were tested for compression with a 50 kN load cell.

2.3 X-ray diffraction analysis

The samples for XRD analysis, from integral parts resulting from the compressive test, were dried and sieved in order to enrich the mortar binder fraction. These samples were afterwards ground to particle size < 106µm. X-ray diffractograms were obtained on a Philips PW3710 X-ray diffractometer, with 35 kV and 45 mA, using Fe-filtered CoKα radiation of wavelength λ=1.7903 Å. Diffractograms were recorded from 3-74 º2θ, in 0.05 º2θ increments with 1 second per increment, in effect 0.05 º2θs^{-1}.

2.4 Thermogravimetric and differential thermal analysis (TG-DTA)

The mortars to be analysed by simultaneous thermal analysis (STA) were dried and ground to particle size < 106µm. The STA analysis was performed in a SETARAM TG-DTA analyser, under argon atmosphere, with heating rate of 10ºC/min, from room temperature up to 1000ºC. Free portlandite content in the samples was determined from the mass loss in the range of 380 – 500ºC, corresponding to portlandite dehydroxilation. The CO_2 content present in the samples was attained in the mass loss range of 500 – 850ºC, which allows knowing its calcite content.

The TG curves were supported by the dTG curves, since the beginning and end of the mass losses are more perceptible.

3. Results

3.1 Flexural and compressive strength

The results obtained with pure lime and with lime-Mk mortars at each curing condition and age are presented in Figure 1. According to the reported results, among pure lime mortars, curing with sea water spray presented the higher strength, particularly at 90 days of age. Among the lime-Mk mortars, the higher results were not so clearly identified by mortars, curing and ages. Pure lime mortars have much higher mechanical behaviour than 9% Mk mortars. In fact air lime-Mk mortars present almost 80% less flexural and compressive strengths. Maritime air spray was the curing condition that led to the higher values for air lime mortar, while for 9% Mk the humid and the potable water spray led to the higher results. Air lime mortar with humid curing is not the mortar with the highest strength values, though it is the only one where both flexural and compressive strength values still increases at ages up to 1 year. For the other mortar/curing conditions often a decrease occurs from 90 days to 1 year of age.

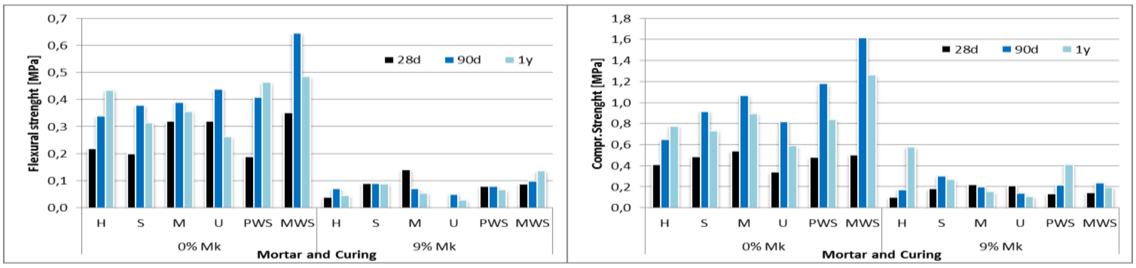

Figure 1: Flexural and compressive resistances at ages of 28, 90 days and 1 year of air lime and air lime-Mk mortars at different curing conditions.

3.2 X-ray diffraction

The XRD patterns of the formulated mortars are presented in figures 2 a) and b), which show the main hydrated phases up to 1 year of curing. The 9% Mk mortar of maritime curing condition at 1 year of ageing is not present because the test samples were destroyed by the weather. As expected, the main hydrated phases formed on mortars without Mk are portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$), while the hydrated phases obtained in 9% Mk mortars are monocarboaluminate ($3CaO.Al_2O_3.CaCO_3.11H_2O$), calcium aluminate hydrated ($Ca_2Al(OH)_7.6.5H_2O$) and hydrocalumite ($Ca_2Al(OH)_{6.5}Cl_{0.5}.3H_2O$). The presence of calcite is verified, which increases with curing time, also the presence of quartz and feldspar is verified since they are constituents of the siliceous sand used in the mortars formulation.

Comparing Figure 2 a) and b), mortars prepared with Mk present a steep decrease in the portlandite content with ageing, which is explained by the consumption of portlandite towards the pozzolanic reaction, as well as for the carbonation reaction. The introduction of Mk seems to delay the carbonation reaction at 28 days, but it increases with ageing in all mortars.

Monocarboaluminate, as described by Arizzi and Cultrone (2012), derives from the reaction between the reactive alumina of Mk and the free portlandite found in the mortars in the presence of CO_3. This mineral occurs in earlier ages (28d) and shows to be very unstable, which may turn into calcium aluminate hydrated or hydrocalumite at older ages (figure 3). This unstable behaviour could be attributed, as described by Silva and Glasser (1993), to the reduction of Ca^{2+} and OH^- ions of the pore solution.

Nevertheless, minor phases were also observed, such as vaterite, aragonite (only in 9% Mk mortar, in Standard cure) and halite, which was expected in maritime water spray cure.

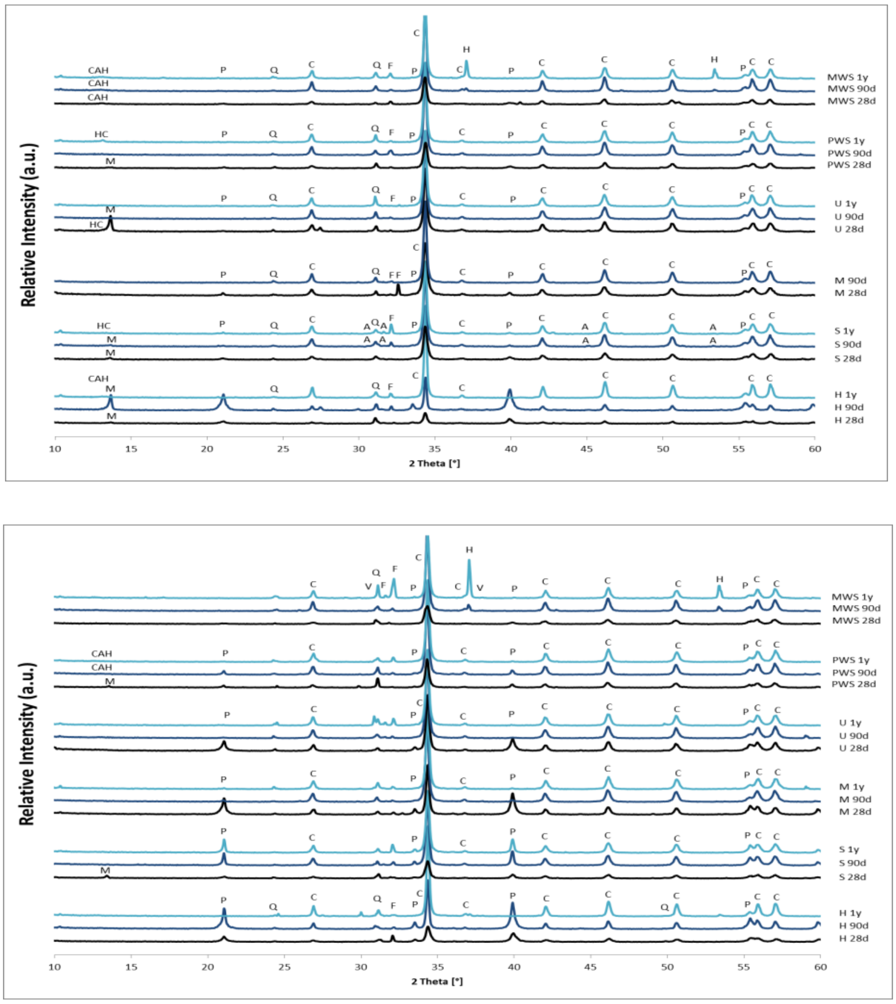

Figure 2: XRD patterns of mortars with a binder/aggregate 1/3 ratio and (above) 0% Mk or (below) 9% Mk (28 days vs. 90 days vs. 1 year of curing); M – Monocarboaluminate ($3CaO.Al_2O_3.CaCO_3.11H_2O$); CAH – Calcium aluminum hydrate ($Ca_2Al(OH)_7.6.5H_2O$); HC – Hydrocalumite ($Ca_2Al(OH)_{6.5}Cl_{0.5}.3H_2O$); P – Portlandite ($Ca(OH)_2$); C – Calcite ($CaCO_3$); Q – Quartz ($SiO_2$); F – Feldspar ($KAlSi_3O_8$); V – Vaterite ($CaCO_3$); A – Aragonite ($CaCO_3$); H – Halite (NaCl).

3.3 Thermal analysis

Figures 3 a) and b) show the DTA charts for the mortars under analysis, which presents 3 main endothermic peaks at the following temperature ranges: ~ 105 - 240ºC, ~ 460ºC, ~ 750ºC, corresponding to the pozzolanic product dehydroxilation, the portlandite dehydroxilation and the carbonates decarboxylation regions, respectively.

Analysing the figures, several aspects can be withdrawn, such as the carbonation reaction which is delayed at 28 days of curing with Mk and it increases with curing time for all mortars. The content of portlandite should also be highlighted; in fact it is viewed to decrease with ageing and with the presence of Mk, except in the case of humid curing condition with 9% Mk, where portlandite presence is remarkable at the age of 28 days.

As expected the endothermic pozzolanic dehydration peaks are more present for 9% Mk mortars.

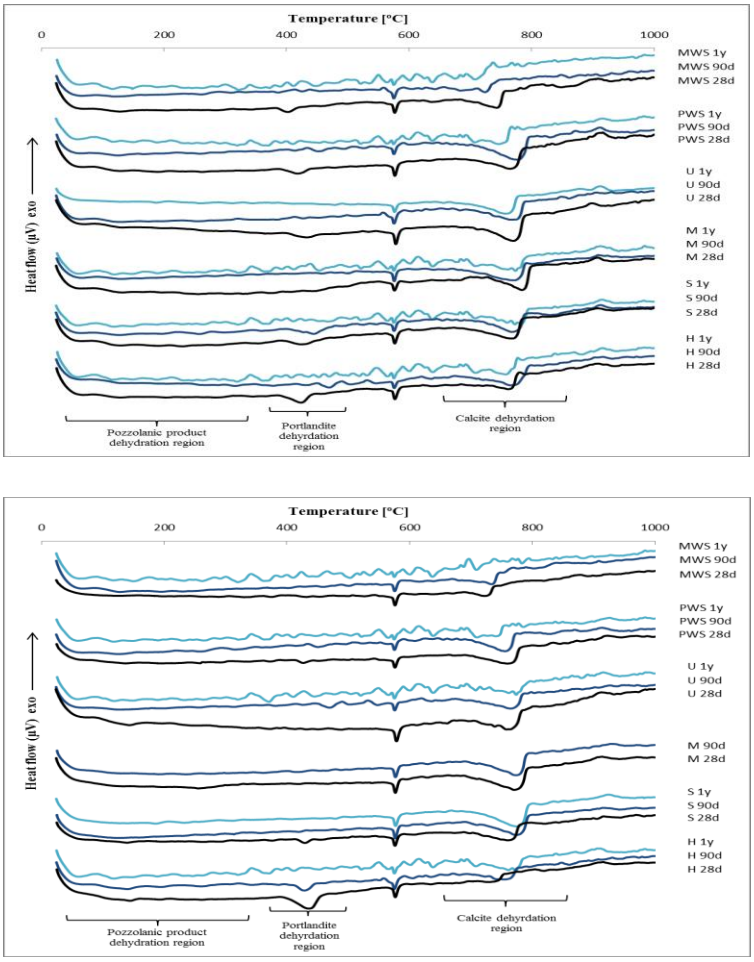

Figure 3: DTA results of 1/3 (binder/aggregate) mortar ratio with (above) 0% Mk and (below) 9% Mk.

3.3.1 Mass losses

To study the evolution of the pozzolanic versus the carbonation reaction, determination of consumed lime content was calculated according to equation 1, respectively:

i) $CH_{poz\ (lime\ consumed\ in\ the\ pozzolanic\ reaction)} = CH_{th} - (CH_f + CH_{carb})$ [Equation 1]

- **CH_{th}** - the amount of lime used in %
- **CH_f** - free portlandite content obtained by Equation 1.1
- **CH_{carb}** – lime carbonated obtained by Equation 1.2

ii) $CH_{f\ (free\ portlandite\ content)} = ML_{(350\text{-}500ºC)} \times MM_{(CH)}/MM_{(H2O)}$ [Equation 1.1.]

- **$ML_{(350\text{-}500ºC)}$** - mass loss attributed to portlandite dehydration in the temperature range 350-500ºC.
- **$MM_{(CH)}$** - molar mass of portlandite
- **$MM_{(H2O)}$** - the molar mass of water

(iii) $CH_{carb(carbonated\ portlandite\ content)} = (ML_{(500\text{-}850ºC)} \times MM_{(CaCO3)}) / (MM_{(CO2)})$ [Equation 1.2]

- **$ML_{(500\text{-}850ºC)}$** - CO_2 mass loss in the temperature range 500-850ºC, corresponding to calcite decarboxylation.

- **MM$_{(CaCO_3)}$** - the molar mass of calcite,
- **MM$_{(CO_2)}$** - the molar mass of carbon dioxide.

The evolution of the lime consumption in terms of the pozzolanic reaction versus the carbonation reaction is illustrated in figure 4.

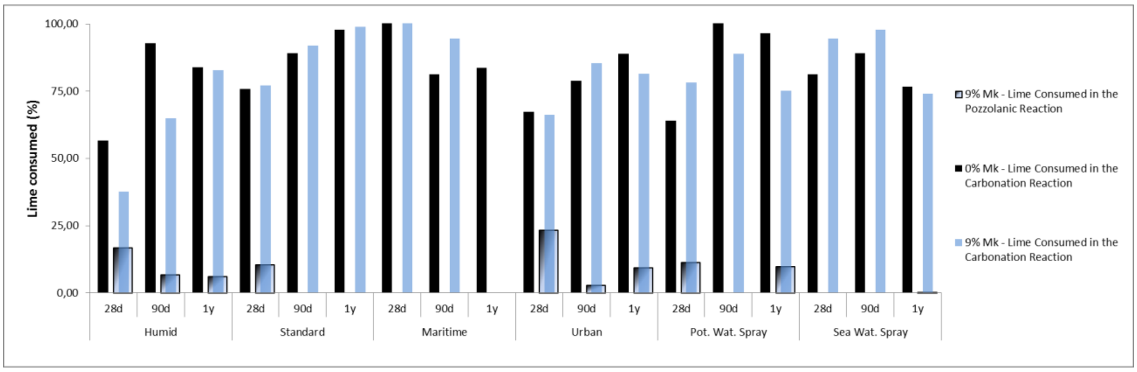

Figure 4: Comparison between the pozzolanic reaction and carbonation reaction in 1/3 (binder/aggregate) mortar ratio with 9% Mk.

Carbonation reaction dominates in all mortars and ageing promotes its increase. Moreover, pozzolanic reaction is weak and mainly evident at 28 days, decreasing with ageing. This result could be related to the instability of the calcium aluminate hydrated compounds formed as shown by XRD analysis (figure 2 b). Humid and urban curing seemed to be the ones where pozzolanic reaction has better results.

4. Conclusions

According to the XRD results the main hydrated phases formed in these air lime-Mk blended mortars are monocarboaluminate, hydrocalumite, calcium aluminate hydrate and portlandite, which are chemically compatible with old renders and masonries. In the meantime, TG-DTA results showed that humid and urban curing revealed the best results in terms of the pozzolanic reaction, occurring mostly at lower curing times (28 days), although carbonation reaction is dominant throughout all ages up to 1 year.

Regarding mechanical behaviour, all the examined air lime-Mk mortars present nearly less 80% flexural and compressive strengths than pure lime mortars. Nevertheless, monocarboaluminate, hydrocalumite and calcium aluminate hydrated seemed to offer better mechanical behaviour amongst these mortars. Recent studies showed that air lime-Mk mortars with a higher binder ratio, for example 1/1 or 1/2 binder/agregate mortar ratios and 30 or 50% Mk (mass% replacement of air lime) at humid curing conditions, have much higher mechanical strength (Gameiro 2013). In the mortars the formation of calcium-silicate hydrates, like stratlingite, can justify the results. From the results it seems that too low amounts of lime replacement by Mk can have a beneficial effect on initial hardening period but can lead to mortars with reduced strength and that the curing conditions for in situ application should be taken into account.

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